

ANALYSIS OF SULFUR FORMS IN ASPHALTS USING SULFUR K-EDGE XAFS SPECTROSCOPY

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Keywords: Asphalt, Sulfur, X-ray Absorption Fine Structure Spectroscopy

ABSTRACT

The sulfur functional groups present in a number of asphalt samples, which varied in total sulfur content from 1.1 wt% to 6.9 wt%, have been investigated by means of sulfur K-edge XAFS spectroscopy. This method, which is based on a least-squares method of analysis of the sulfur XANES spectrum, is capable of quantitatively determining aliphatic sulfur forms, such as sulfides, aromatic sulfur forms, such as thiophenes, and oxidized sulfur forms, such as sulfoxides, sulfones, etc. In the unoxidized asphalt samples examined, oxidized sulfur forms are generally absent, and the principal sulfur form found is thiophenic. However, thiophenic sulfur forms vary from about 54% of the total sulfur to about 78% and there is a weak negative correlation in this trend with total sulfur content. Comparison of sulfur forms in asphalts before and after oxidation treatments shows that only the aliphatic sulfur component oxidizes to sulfoxide.

INTRODUCTION:

One of the many studies of asphalts being conducted under the Strategic Highway Research Program (SHRP) is an investigation of the mechanism of asphalt oxidation to determine those variables that influence oxidative aging. One of the predominant oxidation products found in asphalts is the sulfoxide functional group. Consequently, we are interested in understanding the role that different sulfur forms may play in the oxidation process. In this study, sulfur K-edge X-ray absorption fine structure (XAFS) spectroscopy has been used to characterize the different sulfur forms in asphalts and the changes in these sulfur species on oxidation.

EXPERIMENTAL:

Samples and Oxidation Treatments: All of the asphalt samples were obtained from the SHRP Material Reference Library. Thermal oxidation of the asphalts was conducted at the Western Research Institute. Asphalts were oxidized by the Thin-Film Oven Test followed by additional conditioning for 144 hours at 60°C under 300 psi air in a pressurized oxidation vessel. These two conditioning procedures mimic both short term ageing and the longer term ageing experienced by the pavement in the field.

Chemical oxidation was performed on samples of AAA-1 (Asphalt X) and AAG-1 (Asphalt Y) by dissolving about 1 g of asphalt in 25 ml of cyclohexane, and adding 5-7 equivalents of *t*-BuOOH based on the total sulfur concentration in the asphalt. This mixture was stirred for 4-8 hours at room temperature. The samples were then washed three times with 50

ml volumes of purified water, dried over sodium sulfate, and stripped free of the solvent. Since AAG-1 formed an emulsion during the water washing, sodium bisulfite was added to reduce and remove any residual hydroperoxide.

Sulfur K-edge XAFS Spectroscopy: XAFS spectroscopy at the sulfur K-edge was performed at beam-line X-19A at the National Synchrotron Light Source, Brookhaven National Laboratory. This beam-line is unfocused and all components are in machine vacuum up to the experimental hutch to maximize the intensity of soft X-rays (2-5 keV) reaching the sample. The monochromator consists of a double channel-cut silicon (111) crystal assemblage that can be rotated by means of a precision stepping motor to select a specific range of energies for the spectral scan. Absorption of the X-rays was measured by means of an ion chamber that detects the fluorescent X-rays emitted over a large solid angle in response to the absorption process. For sulfur, absorption of X-rays was measured over the spectral range from 2.4 keV to 2.8 keV; over the X-ray absorption near-edge structure (XANES) region (ca. 2.45 to 2.50 keV), absorption data were collected every 0.08 eV. The ratio of the intensity of the fluorescent X-rays to that of the incident X-rays as a function of X-ray energy constituted the XAFS spectrum. The primary calibration standard employed was elemental sulfur diluted to 5 wt% in a boric acid pellet; the major peak maximum at 2.472 keV was defined as the zero energy point for the XANES spectra shown in this report.

The sulfur K-edge XANES spectra of the asphalt samples were obtained from the raw XAFS spectral data in the usual way (1,2). The sulfur XANES spectra were then analyzed by means of a least-squares fitting program and calibration procedure, which is described in detail elsewhere (1,2). Basically, this program fits the sulfur XANES spectra of fossil fuels and related samples as the sum of an arctangent function and a number of lorentzian/gaussian shaped peaks, which represent the "white lines" (1s - 3p electronic transitions) of specific sulfur functional forms. Although this program was primarily designed for analysis of sulfur forms in coals, the same procedure is actually easier and more precise for the analysis of sulfur in asphalts because the complications due to the presence of pyrite in coal (3,4) are avoided. The precision of the determinations is estimated to be $\pm 5\%$.

RESULTS AND DISCUSSION:

As indicated in Figure 1 (top), most unoxidized asphalt samples can be fit with just two distinct components under the major feature in the XANES spectrum. These two components are interpreted as aliphatic sulfide and thiophene sulfur forms based on peak position systematics (1,5). The small peaks at higher energies represent secondary processes (resonant scattering phenomena) that occur in the same components. For oxidized asphalts (Figure 1, bottom), peaks for oxidized sulfur forms, principally sulfoxide, occur near where these secondary peaks are found. The calibration procedure allows for the different contributions in such cases and oxidized sulfur forms can also be estimated from the sulfur XANES spectrum (1,2).

Representative sulfur K-edge XANES spectra are shown in Figure 2 for some of the asphalt samples investigated in this study. The spectra of all asphalt samples were fit in similar fashion to those shown in Figure 1 and the derived data on percent sulfur in different functional forms are presented in Table 1. In addition, the third derivative spectra were also examined (not shown) and these data confirmed the presence of just two contributions, aliphatic sulfide and thiophene, to the main spectral peak.

Samples that were subjected to oxidation showed the presence of significant sulfoxide. For those samples that were available in both unoxidized and oxidized states, the difference spectrum obtained by subtracting the sulfur XANES spectrum for the oxidized asphalt from that

for the corresponding unoxidized sample was especially revealing (Figure 3). Such difference spectra invariably showed the presence of a positive peak at about 0.3 - 0.5 eV and a negative peak at about 3.0 - 3.5 eV. These peak positions correspond to those for aliphatic sulfide and sulfoxide sulfur forms, respectively. There was little or no difference between the oxidized and unoxidized spectra in the vicinity of 1.2 - 1.5 eV, where the peak for thiophene sulfur is found. It is clear then from this analysis, that the oxidation procedure converts aliphatic sulfur forms to sulfoxide, but does not significantly affect the thiophenic sulfur forms. It should be noted that whereas approximately 50% of the aliphatic sulfur in sample AAG-1 was converted to sulfoxide, significantly lesser amounts were oxidized in samples AAA-1 and AAK-1 because of their greater initial sulfide contents.

Comparison of the sulfur K-edge XAFS data with sulfur ESCA spectral analysis for AAA-1 showed reasonably good agreement for the sulfide to thiophene sulfur ratio [6].

XAFS analysis of the sulfur forms in thermally oxidized AAA-1, AAG-1, and AAK-1 indicate formation of varying proportions of sulfoxide derived only from sulfide sulfur. About 32 and 14% of AAA-1 and AAK-1 sulfides, respectively, disappear on thermal oxidation, part of which is accounted for by formation of sulfoxide. However in AAG-1, 51% of the sulfide oxidizes to give the expected amount of additional sulfoxide. No other oxidized sulfur species was observed in these samples. ESCA spectra of oxidized asphalt AAA-1 [6] showed that almost 40% of the sulfide sulfur disappeared in 48 hours at 110°C, in reasonable agreement with the XAFS result for AAA-1. Both spectral methods showed significant deficits between sulfoxide formed compared to sulfide oxidized in AAA-1.

The chemically oxidized sample, Asphalt Y (AAG-1), shows a high proportion of sulfate in the XAFS spectrum (Figure 4). This is probably attributable to the use of bisulfite to reduce residual t-BuOOH during clean up.

Information was available on the total sulfur contents of the asphalts and plots were prepared of the XANES derived data on sulfur forms against total sulfur for the unoxidized samples. As indicated in Figure 5 and also in Table 1, these data show that thiophenic sulfur in the asphalts averages approximately 66% of the total sulfur; however, there appears to be a weak negative correlation between % sulfur as thiophene and wt% total sulfur, such that the percentage of sulfur as thiophene varies from a high of 78% in low-sulfur asphalts to about 54% in high-sulfur asphalts. As thiophene is not affected by oxidation, these observations apply regardless of whether the asphalt is oxidized or not.

CONCLUSIONS:

A calibrated, least-squares method of analysis of sulfur K-edge XANES spectra has been used for the direct, non-destructive determination of sulfur species in asphalts. Although specific sulfur compounds are not identified, the technique is valuable for quantitatively determining the distribution of sulfur among various organic sulfur functionalities. In this study of eight asphalt samples, thiophene-like aromatic sulfur forms were found to constitute on average about two-thirds of the sulfur, with the remainder being aliphatic sulfide or oxidized sulfur forms. Samples oxidized by either a thermal or a chemical oxidation treatment showed that the aliphatic sulfur forms were partially oxidized to sulfoxide, and that the thiophenic sulfur forms were unaltered.

Acknowledgements:

The sulfur XAFS spectra were obtained at the National Synchrotron Light Source at Brookhaven National Laboratory, which is supported by the U.S. Department of Energy.

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TABLE 1

Quantitative Analysis of Sulfur K-edge XANES Spectra
of Thirteen Asphalt Samples

Sample I.D.	Wt% Sulfur in Asphalt	% Sulfur in Sulfur Functional Groups*			
		Sulfide	Thiophene	Sulfoxide	Other
AAA-1	5.5	40	60	--	--
AAA-1 oxid.	5.3	27	67	6	--
AAB-1	4.7	31	69	--	--
AAC-1	1.9	25	75	--	--
AAD-1	6.9	46	54	--	--
AAF-1	3.5	28	72	--	--
AAG-1	1.3	33	59	8	--
AAG-1 oxid.	1.1	15	60	25	--
AAK-1	6.4	36	64	--	--
AAK-1 oxid.	5.9	31	62	7	--
AAM-1	1.2	17	78	5	--
Asph-X (AAA-1)†	---	10	63	27	--
Asph-Y (AAG-1)†	---	0	53	17	3 Sulfone 27 Sulfate

*Determinations of %Sulfur in Sulfur Functional Groups are accurate to $\pm 5\%$.

†Chemically oxidized asphalts.

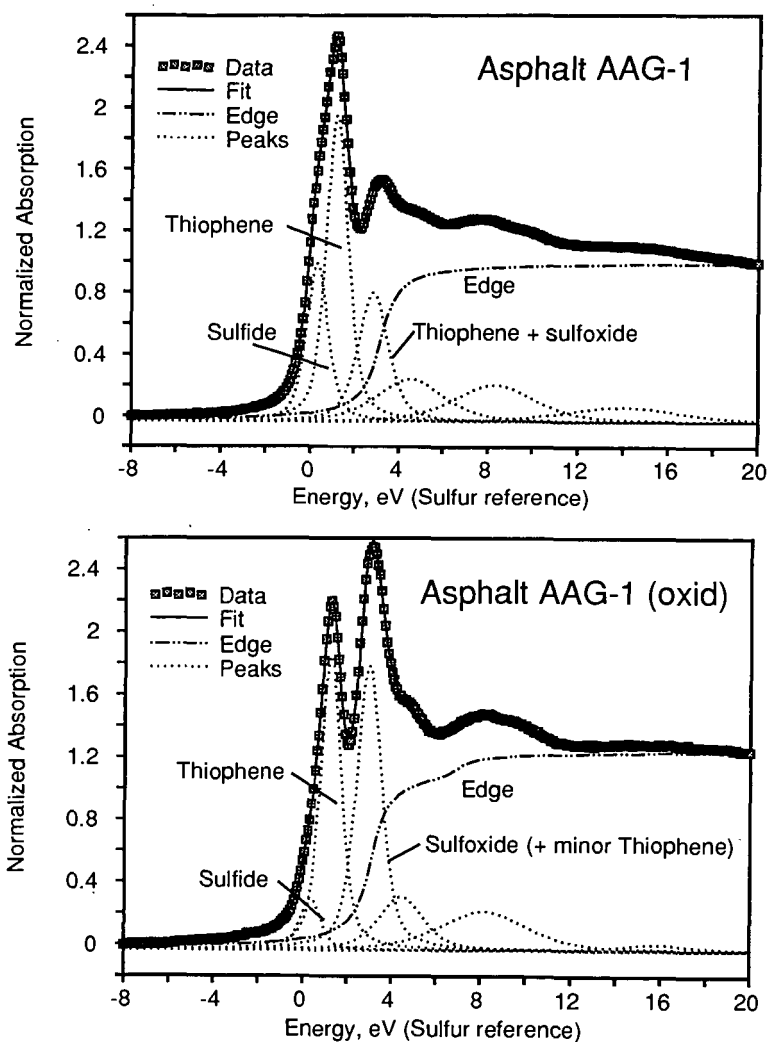


Figure 1: Least-squares fitted sulfur K-edge XANES spectra of asphalt sample AAG-1 before (top) and after (bottom) oxidation.

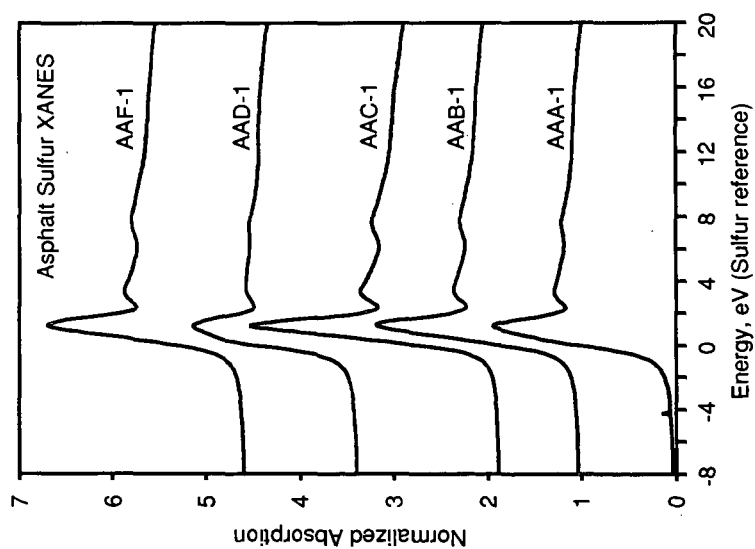


Figure 2: Sulfur XANES spectra of selected asphalt samples.

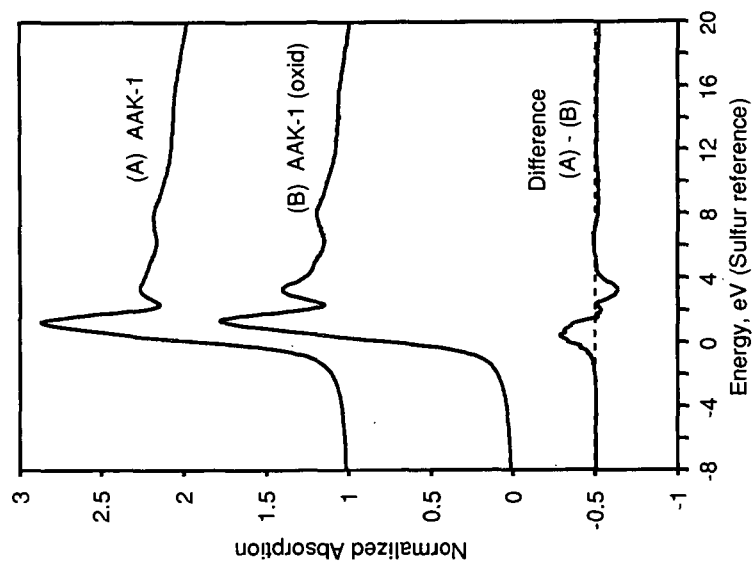


Figure 3: Sulfur XANES and difference spectrum for asphalt samples AAK-1 and AAK-1 (oxid).

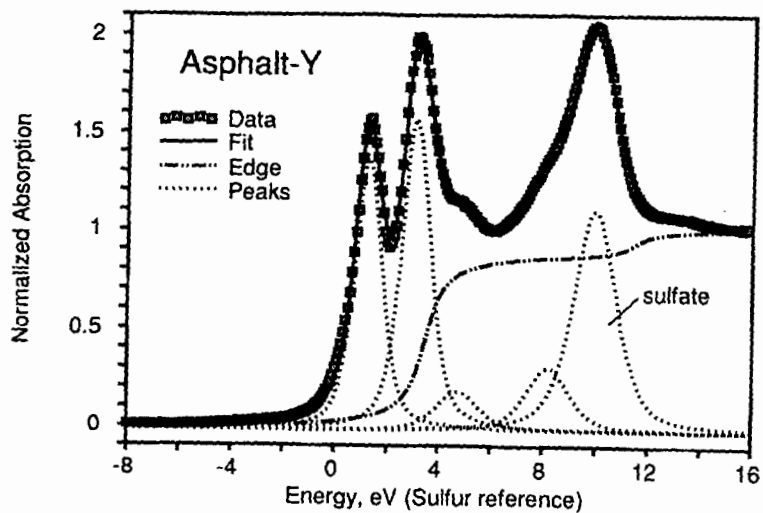


Figure 4: Sulfur K-edge XANES spectrum of chemically oxidized asphalt sample, AAG-1.

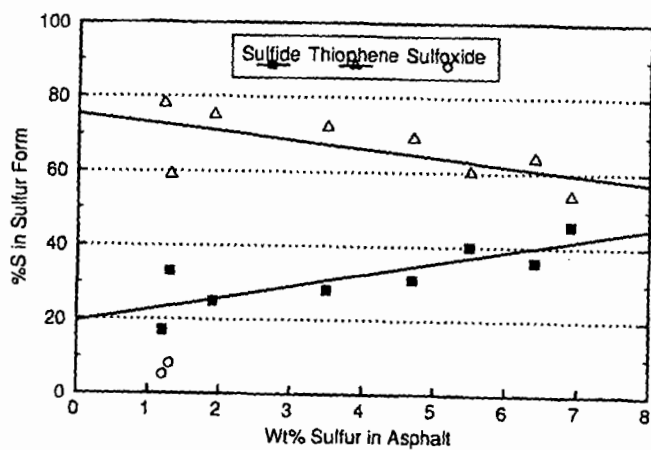


Figure 5: Plot of %S in specific sulfur form against wt% S in asphalt for the eight unoxidized asphalt samples.